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Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment

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ABSTRACT

Pretreatment of lignocellulosic biomass is of the utmost importance for the development of bioethanol because of the abundance and low cost of lignocelluloses. To figure out the hydrolysis characteristics of sugarcane bagasse in a microwave irradiation environment, the biomass is pretreated by a dilute sulfuric acid solution at 180 °C for 30 min, with the concentration ranging from 0 to 0.02 M. A variety of analyses, including fiber analysis, TGA, XRD, FTIR and HPLC, are employed to aid in understanding the physical and chemical characteristics of residual solid particles and solutions. A higher concentration is conducive to destroying bagasse; however, the buffering capacity possessed by the biomass is also observed in the pretreatment. The experimental results indicate that around 40–44 wt% of bagasse is degraded from the pretreatment in which around 80–98% of hemicellulose is hydrolyzed. In contrast, crystalline cellulose and lignin are hardly affected by the pretreatment. The maximum yields of xylose and glucose as well as the minimum furfural selectivity occur at the acid concentration of 0.005 M. Consequently, the aforementioned concentration is recommended for bagasse pretreatment and bioethanol production.

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1. Introduction

Bioethanol is an important fuel nowadays because it has been widely blended with oil and consumed in internal combustion engines for the power of vehicles [1–4]. Currently, most of the bioethanol is produced from maize or sugarcane [5]. When bioethanol is produced from the aforementioned feedstocks, the raw materials account for around 40–70% of the production cost [6]. For the mass production of bioethanol, it is always desirable to use cheaper and more abundant substrates. Lignocelluloses, which can be obtained from the wastes of forest industry, energy crops, agricultural residues and grass, have been considered as attractive feedstocks for the prospective production of bioethanol, because of its low cost, availability in large quantities and low risk of causing food storage [7,8].

Lignocelluloses consist mainly of hemicelluloses, cellulose and lignin [9,10]. Hemicelluloses are branched polysaccharides containing sugar residues, such as xylose, mannose, galactose, glucose, arabinose and glucuronic acid [11]. Cellulose is a linear polymer of glucose in which crystalline and amorphous structures are contained [12]; lignin is an amorphous polymer made up of aromatic derivatives [13]. In order to produce bioethanol from lignocelluloses, it is essential to obtain fermentable sugar from hemicellulose and cellulose, especially for the latter. However, by virtue of lignocelluloses featured by recalcitrance in nature, the process of biomass pretreatment is required [14]. The purposes of pretreatment are to remove hemicellulose and lignin, decrease crystalline cellulose and increase the surface area of the materials [15], thereby facilitating the subsequent enzymatic hydrolysis. As a matter of fact, studies have suggested that pretreatment is the most important step for bioethanol production from lignocelluloses in that it defines the extent to and cost at which the carbohydrates of hemicellulose and cellulose can be converted to bioethanol [16].

As far as biomass pretreatment is concerned, a number of methods, such as mechanical pretreatment, alkali or acid pretreatment, steam explosion, ammonia fiber explosion, hot water, supercritical CO_2 treatment, ozone pretreatment and biological pretreatment, have been developed [16]. Alkaline pretreatment has received a lot of attention lately because it can remove lignin from biomass, thus improving the reactivity of the remaining polysaccharides and removing acetyl groups and various uronic acid substitutions on hemicellulose. In the study of Fuentes et al. [17] upon sugarcane bagasse pretreatment with lime, they found that the maximum glucose yield was 228.45 mg (g raw biomass)$^{-1}$, corresponding to 409.9 mg (g raw biomass of total reducing sugars)$^{-1}$, with the pretreatment performed at 90 °C, for 90 h, and with a lime loading of 0.4 g (g dry biomass)$^{-1}$. Rodrigues et al. [18] focused on the potential of microwave-assisted alkali pretreatment to improve the rupture of the recalcitrant structures of the cashew able bagasse. With the alkali concentration of 0.2 and 1.0 mol L^{-1}, solid percentage of

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16% (w/v) and enzyme load of 30 FPU $g_{CAB\text{-}M}{}^{-1}$, pretreatment time and microwave power had no significant effect on glucose concentration. Despite the advantages of alkali pretreatment utilizing lower temperatures and pressures compared to other pretreatment technologies, the pretreatment time is measured in terms of hours or days rather than minutes or seconds.

Among the developed methods, the pretreatment using dilute sulfuric acid has been thought of as one of the most cost-effective methods [19,20]. To achieve a dilute acid pretreatment, the mixture of biomass and dilute acid solution is usually controlled at a moderate temperature by means of conventional heating [21–23]. In conventional conduction and convection heating, thermal energy is delivered through superficial heat transfer. In addition to conventional heating, microwave-assisted heating is another effective route to pretreat biomass. In microwave-heating processes, materials containing dielectrics are heated by converting microwave irradiation through molecular interactions in electromagnetic fields [24], that is, the electromagnetic energy is converted into thermal energy through dielectric heating. Moreover, the electromagnetic field used in microwaves may create non-thermal effects that also accelerate the destruction of crystal structures [25].

In the study of Palmarola-Adrados et al. [26], they pretreated starch-free wheat fibers in dilute sulfuric acid solutions using microwave heating; it was illustrated that the biomass pretreatment with microwave heating was able to give a higher sugar yield compared to steam explosion. Hu et al. [27] used a radio-frequency-assisted (RF-assisted) heating method to pretreat switchgrass in a NaOH solution. They mentioned that the RF-assisted heating resulted in a higher xylose yield than the conventional heating. In addition, the enzymatic hydrolysis of RF-treated solids led to a higher glucose yield than the corresponding value obtained from the conventional heating. Li et al. [28] carried out the pretreatment of swine manure in sulfuric acid solutions heated by microwaves; it was outlined that microwave irradiation could lead to a higher yield of reducing sugar, shorter reaction time and lower energy consumption so that it was a suitable technique for the saccharification process of swine manure. Zhao et al. [29] used a NaOH solution to pretreat rice hulls in a microwave environment; they mentioned that the increased accessibility of the substrates by microwave pretreatment was mainly achieved by the rupture of the rigid structure of rice hulls, and the reducing sugar content was increased by 13% compared with that of rice hulls without pretreatment. In the study of Nikolić et al. [30], microwaves and ultrasound were individually employed to pretreat corn meal. It was reported that the application of microwave pretreatment resulted in higher yields of glucose and bioethanol when compared to the ultrasound pretreatment. They also pointed out that the application of microwave pretreatment could decrease the time of simultaneous saccharification and fermentation, thereby effectively reducing the production cost of bioethanol. In the study of Lu et al. [31], they also pointed out that, unlike conventional heating, microwaves generate higher power densities, enabling higher production rates and lower production costs.

From the foregoing literature, it is evident that microwave heating is an effective and promising method to pretreat biomass for bioethanol production. To understand the impact of microwaves on the disruption of biomass structure, bagasse pretreated via microwave-assisted heating in a dilute sulfuric acid solution (0.2 M) has been preliminarily performed in a previous study [32]. It was found that an increase in reaction temperature intensified the destruction of the lignocellulosic structure of bagasse in a significant way and the pretreated bagasse particles were simultaneously characterized by fragmentation and swelling. Unfortunately, the influence of dilute acid concentration on the disruption of biomass structure and the analysis of the liquid phase were absent. It is known that dilute acid pretreatment is able to convert hemicellulose contained in lignocellulosic biomass to soluble sugars and facilitates the subsequent enzymatic hydrolysis of cellulose [16,20,33]. However, the hydrolysis of polysaccharides also leads to the formation of sugar degradation products, namely, inhibitors, such as furfural and 5-hydroxymethylfurfural (HMF) [21]. Degradation products not only reduce the yields of sugar monomers but also act as fermentation inhibitors. To produce fermentable hydrolysates and prevent a high loss in sugar yields, it is therefore necessary to choose reaction conditions that keep the generation of inhibitors at a lower level. To date, many efforts are being done to improve processes and develop new technologies so as to achieve further conversion of available sugars from sugarcane bagasse. However, the work is currently being done at laboratory and pilot plant scales and practical applications in industries remain absence. More efforts for prospective applications are required. For this reason, the influence of acid concentration on the yields of hemicellulosic and cellulosic sugars from sugarcane bagasse and the formation of furfural and HMF in a microwave irradiation environment will be explored in the present study. Particular attention is paid to the pretreatment with low sulfuric acid concentrations and optimum operating conditions are suggested.

2. Experimental

2.1. Raw material preparation and standards

Bagasse obtained from Taiwan Sugar Corporation in Tainan, Taiwan, was selected as the raw material to be studied. The bagasse was dried in an oven with the temperature of 105 °C for 24 h to remove the moisture in the law material. Then, the dried bagasse was grinded and sieved to the maximum particle size of 40 mesh (=0.42 mm). Subsequently, the grinded bagasse particles were placed in sealed plastic bags and stored in a desiccator at room temperature until experiments were carried out. In this study, three standards of hemicellulose, cellulose and lignin, were also analyzed for comparisons; they were purchased from SIGMA (X4252), Lancaster (A17730) and TCI (L0045), respectively.

2.2. Reaction system

The schematic of the pretreatment system is demonstrated in Fig. 1 in which a gas supply unit, a heating and power controller unit, a reactor and a pressure control unit were included. In the gas supply unit, nitrogen was stored in a cylinder for leak test and system purge. The heating and power control unit consisted of a microwave oven, a thermocouple and a power controller. The microwave oven was operated at a frequency of 2.45 GHz and its maximum power was 900 W. The signal from the thermocouple was sent to the power controller for controlling power output. The current output from the power controller was fixed at 10A to prevent damaging the oven. The reactor was a vessel made up of Teflon with the volume of 625 ml (50 mm i.d. × 318 mm length). The vessel was covered by a stainless steel cap and only part of the vessel's volume (450 ml) was exposed to microwave irradiation. The pressure control unit was composed of a pressure control switch, a pressure gauge and a pressure valve. The pressure control switch was utilized for controlling the temperature (or pressure) in the reactor; the pressure gauge was used to monitor the pressure and the pressure valve was mounted at the end of pipe for safety.

2.3. Experimental procedure

In each experimental run, 10 g bagasse sample was mixed with 100 ml dilute sulfuric acid solution (25 °C) in the reactor. The

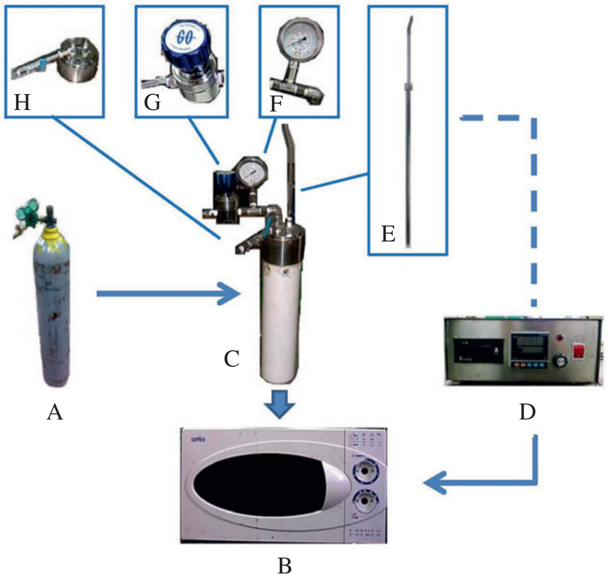

Fig. 1. A schematic of bagasse pretreatment system: (A) nitrogen, (B) microwave oven, (C) reactor, (D) power controller (E) thermocouple, (F) pressure gauge, (G) pressure control switch, and (H) pressure valve.

solid–liquid mixtures were heated by microwaves to the target temperature of 180 °C followed by keeping the temperature for 30 min. In the course of heating and holding temperature, the power from the oven was outputted continuously. After implementing heating, the power controller was turn off and the mixtures were naturally cooled to room temperature. Then, the pretreated mixtures were separated by filter papers (5 μm) into solid particles and liquid solutions. The solid particles were washed by deionized water (1000 ml) to remove the acid remained on the residues so as to cease the possible further reaction of the acid on the materials. Subsequently, the particles were placed in an oven with temperature of 105 °C for 24 h to dry the samples. Eventually, the dried solid residues were analyzed by a variety of instruments to figure out their properties. With regard to the liquid solutions, they were neutralized by a sodium hydroxide solution (2 M). Afterward, they were analyzed to detect the concentrations of soluble sugars and inhibitors.

2.4. Material analysis and experimental quality

The chemical components in the raw bagasse and the pretreated materials, consisting mainly of hemicellulose, cellulose and lignin, were analyzed by determining the neutral detergent fiber (NDF) and the acid detergent fiber (ADF), followed by treating ADF through concentrated H_2SO_4 and measuring ash [34]. Regarding the particle characteristics of the raw bagasse and pretreated materials, such as surface structure, thermal behavior, constituent and crystal structure, they were explored via utilizing a scanning electron microscope (SEM, FEI Quanta 200 ESEM), a thermogravimetry (TG, PerkinElmer Diamond TG/DTA), a Fourier transform infrared spectrometry (FTIR, PerkinElmer/Spectrum 100) and an X-ray diffractometer (XRD, Rigaku Mini Flex II). The liquid solutions were analyzed by a high-performance liquid chromatography (HPLC) equipped with a RI (refractive index) detector and a UV detector. The concentrations of glucose and xylose were measured by the RI detector and a SUPELCOSTL LC-NH2 column using a solution of $CH_3CN:H_2O = 80:20$ (v/v) with the flow rate of 1.3 ml min^{-1} as the mobile phase. Alternatively, furfural and HMF were detected by the UV detector at 272 nm along with a SUPELCOSTL LC-8 column using a solution of $CH_3OH:H_2O:CH_3COOH = 79:20:1$ (v/v) with the flow rate of 1 ml min^{-1} as the mobile phase. Regarding the experimental quality, the pretreatments of raw bagasse at various sulfuric acid concentrations were carried out at least twice to guarantee that the results could be reproduced. As a result, it was found that the relative differences of the fiber analyses of the raw bagasse and pretreated materials were below 10%, revealing that the quality of the experiments was reliable.

3. Results and discussion

As illustrated earlier, dilute sulfuric acid pretreatment has been considered as one of the most cost-effective method for bioethanol production from lignocelluloses. However, by virtue of the addition of acid, the drawbacks accompanied with the dilute acid pretreatment include the requirements of corrosion-resistant materials and neutralization prior to fermentation [26]. Consequently, a lower acid concentration is more feasible for the operation of pretreatment. For this reason, the concentrations of sulfuric acid ranging from 0 to 0.02 M are adopted in the present study. Detailed operating conditions of pretreatment are listed in Table 1.

3.1. Impact of pretreatment on bagasse and solution

From the distribution of solid residue shown in Fig. 2, it can be clearly observed that increasing acid concentration decreases the weight of solid residue to a certain extent. For the case without addition of sulfuric acid, the residual solid is around 60 wt%, whereas it is 56.6 wt% for the acid solution of 0.02 M. It is thus recognized that around 40–44 wt% of bagasse is degraded from the pretreatment. Scanning electron microscope (SEM) images of the raw bagasse and the pretreated samples at four different acid concentrations are shown in Fig. 2 as well. For the raw bagasse, its surface is relatively complete and compact. After undergoing the pretreatment, the bagasse is damaged to a certain extent so that some materials peel off from the surface (0 and 0.005 M) and some tiny holes are exhibited on the surface (0.01 M). With higher acid concentration (0.015 M), the biomass structure is even featured by a tubular configuration.

With attention paid to the liquid phase, Fig. 3 displays the distributions of pH value of the solutions before and after the pretreatment. For the case of 0 M, the pH value of the solution drops to a great extent after the pretreatment. Specifically, the pH values of the solution prior to and after the pretreatment are 6.43 and 3.64, respectively. This is attributed to the release of organic acids, such as formic acid, acetic acid and lactic acid [35], from the bagasse while the biomass is degraded from the pretreatment. On the other hand, it is of interest that the pH value of the solution become higher after the dilute acid pretreatment is practiced. This arises from the fact that biomass generally possesses buffering capacity which can prevent acid production and make the pretreatment less severe [36]. As a whole, the higher the initial acid concentration, the lower the final pH value of the solution. This implies that increasing acid concentration is conducive to the destruction of the bagasse even though the buffering capacity is exhibited by the biomass.

3.2. Constituent and thermogravimetric analyses

In examining the fiber analyses shown in Table 2, it can be seen that the relative content of hemicellulose decreases from 29.92 to 10.09 wt% when the bagasse is pretreated in the neutral solution (i.e. 0 M). An increase in acid concentration intensifies the depletion of hemicellulose so that the relative content of hemicellulose drops to around 1% once the acid concentration is larger than or equal to 0.015 M. Accordingly, it is realized that 79.8 and

Table 1
Operating conditions of dilute sulfuric acid pretreatment.

Bagasse (g)	Temperature (°C)	Soaking time (min)	H_2SO_4 (M)	Water (ml)	H_2SO_4[a] (ml)
10	180	30	0	100	0
			0.0025	99.75	0.25
			0.005	99.5	0.5
			0.0075	99.25	0.75
			0.01	99	1
			0.0125	98.75	1.25
			0.015	98.5	1.5
			0.02	98	2

[a] The concentration of H_2SO_4 is 1 M.

97.8 wt% of hemicellulose contained in the raw bagasse are hydrolyzed from the solutions of 0 and 0.02 M, respectively. Unlike hemicellulose, the relative contents of cellulose and lignin rise with increasing acid concentration, revealing that the two constituents possess the capability of resistance to the pretreatment of dilute acid solution along with a high temperature environment (180 °C). However, once the acid concentration increases from 0.0125 to 0.015 M, it is worthy of note that the relative content of cellulose declines a bit. This reflects that cellulose is also affected by the pretreatment. With regard to lignin, similar behavior is also exhibited when the acid concentration is lifted from 0.015 to 0.02 M. From the results obtained in Fig. 2 and Table 2, it can be summarized that the solid depletion from the pretreatment is mainly due to the degradation of hemicellulose.

Subsequently, the thermogravimetric analyses (TGA) and derivative thermogravimetric (DTG) analyses of the raw bagasse and pretreated materials are displayed in Fig. 4. From the TGA distributions (Fig. 4a), it can be seen that the difference among the pretreated materials is slight, whereas there is a pronounced difference between the raw bagasse and the pretreated samples. This indicates that the pretreatment has a significant influence on the raw bagasse, but the thermal degradation of the pretreated bagasse is insensitive to the acid concentration. With further exanimation upon the DTG curves (Fig. 4b), the distribution of the raw bagasse is characterized by a double-peak distribution. The first and the second peaks, developing at 313 and 365 °C, respectively, represent the thermal degradations of hemicellulose and cellulose in the bagasse. Once the bagasse experiences pretreatment, the first peak disappears, suggesting that hemicellulose has been removed to a great extent.

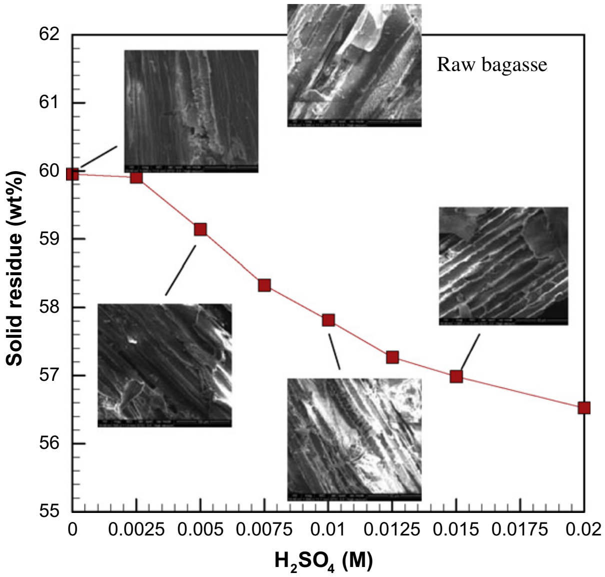

Fig. 2. Profiles of weight percentage of residual solid after bagasse pretreatment and SEM images (×1000).

The DTG curves also reveal that the impact of the pretreatment on cellulose is slight in that the variation in the second peak is insignificant. These results are consistent with the analyses shown in Table 2.

3.3. XRD and FTIR analyses

To proceed further into the recognition of cellulose structure, the XRD patterns of the raw bagasse and the pretreated materials are sketched in Fig. 5. It has been reported [22,37] that a major diffraction peak of cellulose crystallographic plane can be identified for 2θ in the range of 22–23°. For the raw bagasse, the crystalline structure is not notable, probably due to the coverage of cellulose by hemicellulose and lignin. For the pretreatments with the acid concentrations of 0, 0.01 and 0.02 M, the crystalline cellulose of the pretreated materials is clearly exhibited. The patterns also reflect that the crystalline structure of cellulose is hardly destroyed by the pretreatments, even though the temperature is as high as 180 °C along with the acid concentration of 0.02 M.

Upon inspection of the FTIR spectrum of hemicellulose standard shown in Fig. 6, the characteristic peaks at the wave numbers of 897, 1043, 1164 and 1248 cm^{-1} can be identified clearly. These peaks are consistent with the observations of Ren et al. [38]. For the raw bagasse, the four peaks can still be pointed out. However, when the spectra of the pretreated materials are examined, it is evident that the peaks of the pretreated materials at 1043 and 1248 cm^{-1} wither in a significant way. It follows that the constituent of hemicellulose in the bagasse is consumed greatly, as discussed in Table 2 and Fig. 4. It is noted that a sharp band develops at 897 cm^{-1}, attributing to β-glycosidic linkages between sugar

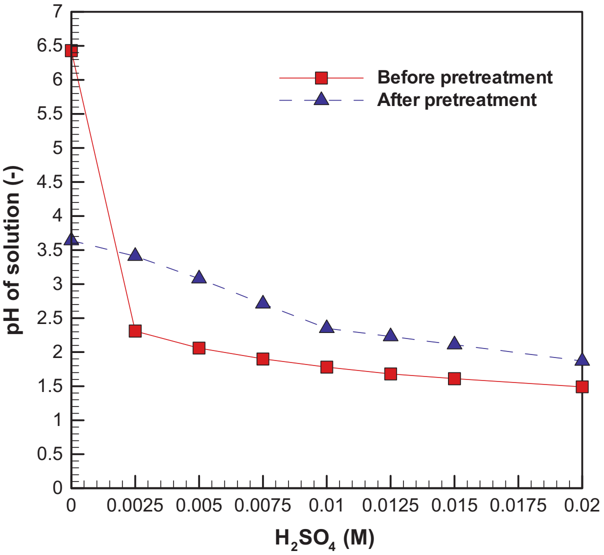

Fig. 3. Distributions of pH value of solutions before and after the pretreatment.

Table 2
Fiber analyses of raw bagasse and pretreated materials.

Material	H_2SO_4 (M)	Hemicellulose (wt%)	Cellulose (wt%)	Lignin (wt%)	Others (wt%)
Raw bagasse		29.92	48.45	17.12	4.51
Pretreated bagasse	0	10.09	58.53	21.42	9.96
	0.0025	4.83	60.97	19.40	14.8
	0.005	3.84	59.66	23.72	12.78
	0.0075	3.8	60.69	23.1	12.41
	0.01	2.52	62.21	23.83	11.44
	0.0125	1.83	62.59	25.86	9.72
	0.015	0.73	59.58	28.9	10.79
	0.02	1.15	57.82	27.25	13.78

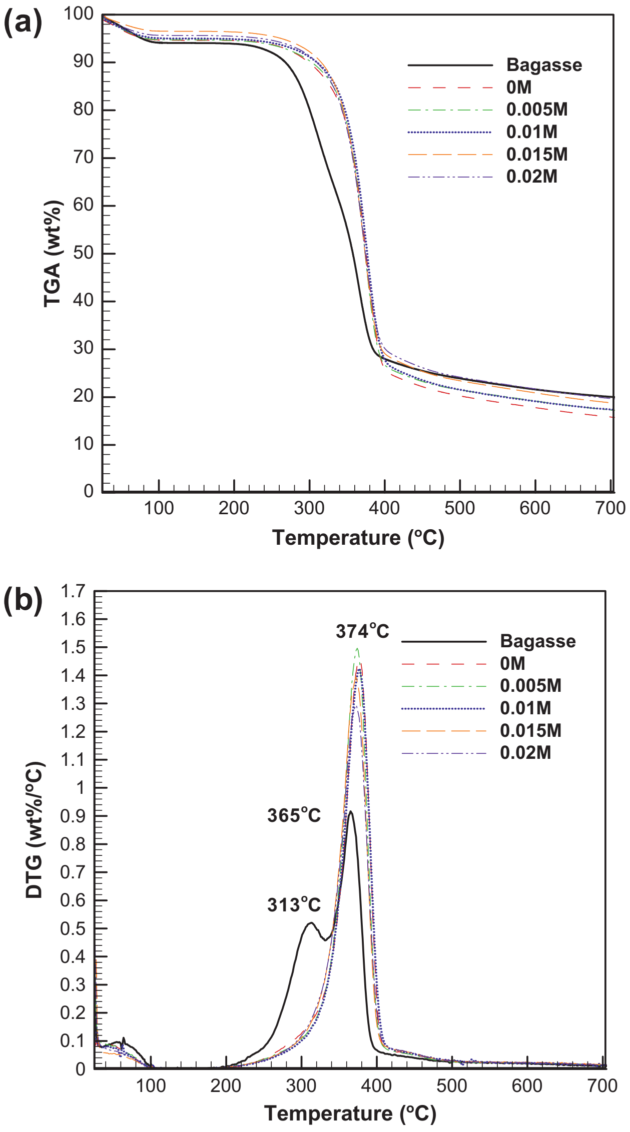

Fig. 4. Distributions of: (a) TGA and (b) DTG of the raw bagasse and pretreated materials at various sulfuric acid concentrations.

units [32,38]. This indicates that xylose residues, which form the backbone of the hemicellulose of the bagasse, are linked by β-form bonds. In the study of Liu et al. [12], it has been highlighted that the absorbance at 897, 1030, 1064, 1106 and 1168 cm^{-1} can be identified for cellulose with the wave number ranging from 800 to 1300 cm^{-1}. In Fig. 7, the aforementioned peaks are also obtained. For the raw bagasse, the peaks at 1064 and 1106 cm^{-1} are not notable. However, once the bagasse is pretreated, the two peaks are exhibited. Again, this reflects that the pretreatment is able to remove hemicellulose so as to enhance the characteristic of cellulose contained in the bagasse. Considering lignin, it can be identified from the FTIR spectrum at the wave numbers of 1420, 1462, 1511 and 1599 cm^{-1}, as shown in Fig. 8. These peaks are very close to the results of Sun et al. [39]. Whether the bagasse is pretreated or not, the four peaks are always observed, revealing that lignin contained in the bagasse is hardly affected by the pretreatments. On the other hand, it is noteworthy that the peaks at 1511 and 1599 cm^{-1} have a trend to be amplified compared to those of the raw bagasse.

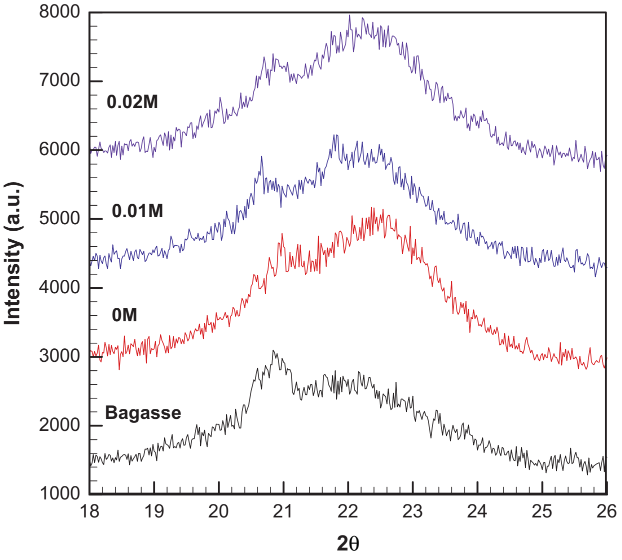

Fig. 5. XRD patterns of raw bagasse and pretreated materials at various sulfuric acid concentrations.

3.4. Yields and conversions of sugars and inhibitors

It has been known that xylose comes from the hydrolysis of hemicellulose and the pretreatment can further break xylose down to form furfural [16]. Similarly, glucose stems mainly from cellulose hydrolysis and it can be further converted to HMF [40]. To recognize the formation characteristics of sugars and inhibitors, the concentrations and yields of two sugars (i.e. xylose and glucose) and two inhibitors (furfural and HMF) are presented in Figs. 9 and 10, whereas their conversions and selectivities are plotted in Fig. 11. The definitions of yield, conversion and selectivity are tabulated in Table 3.

Fig. 9a depicts that the concentrations of xylose and furfural are in the ranges of 0.42–1.25 wt% and 0.075–0.29 wt%, respectively. It is worthy of note that the maximum yield (=38.3%) of xylose occurs at 0.005 M rather than 0.02 M (Fig. 9b). Physically, this means that 38.3 wt% of degraded hemicellulose becomes xylose. Unlike the profile of xylose, a higher acid concentration causes a higher yield

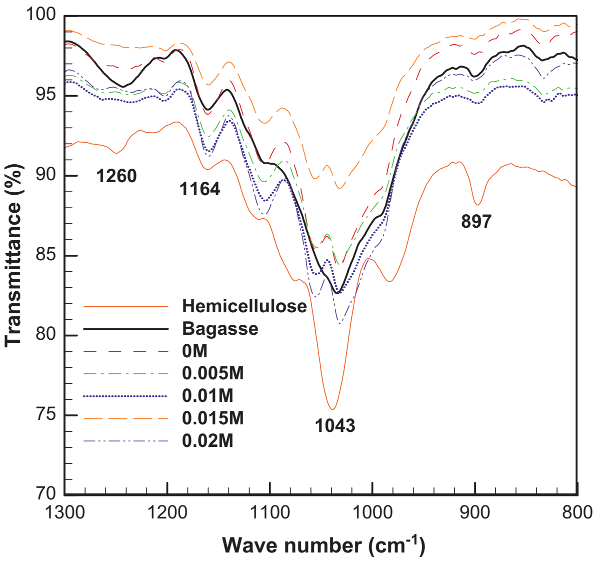

Fig. 6. FTIR spectra of raw bagasse, hemicellulose and pretreated materials at various sulfuric acid concentrations.

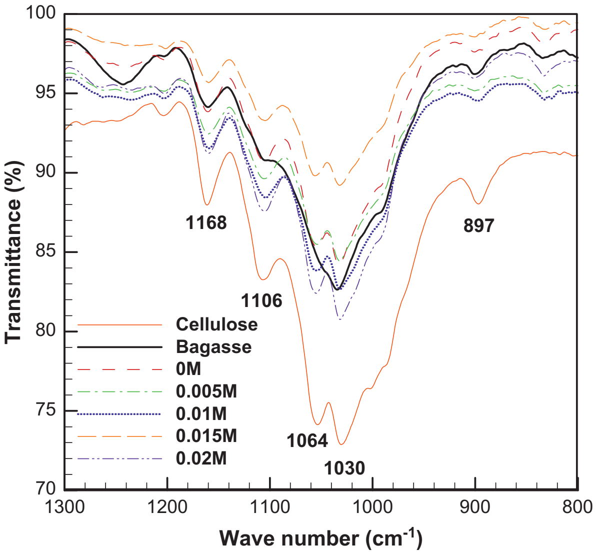

Fig. 7. FTIR spectra of raw bagasse, cellulose and pretreated materials at various sulfuric acid concentrations.

of furfural, implying that more xylose is consumed for the generation of furfural. This is the reason that the xylose yield declines when the acid concentration increases from 0.005 to 0.02 M. When the acid concentration is 0.02 M, the furfural yield is even higher than the xylose one. It is thus addressed that the preceding concentration is not recommended for bagasse pretreatment. With emphasis shifted to glucose and HMF, Fig. 10a indicates that their concentrations are much lower than those of xylose and furfural. Meanwhile, the pronounced difference between the yields of glucose and HMF indicates that it is relatively difficult to form the latter from the degradation of the former. In regard to the yields of glucose and HMF, the former and the latter are less than 6.5% and 1.2%, respectively (Fig. 10b). Similar to xylose, it can be seen that the maximum yield (=6.44%) of glucose also takes place at 0.005 M. It is inferred that the generated glucose partially stems from the hydrolysis of amorphous cellulose [41] and partially from hemicellulose [40]. In the present study with the condition of 0.005 M, the concentrations of xylose and glucose in the solution are 12.5 and 3.3 g L^{-1}, respec-

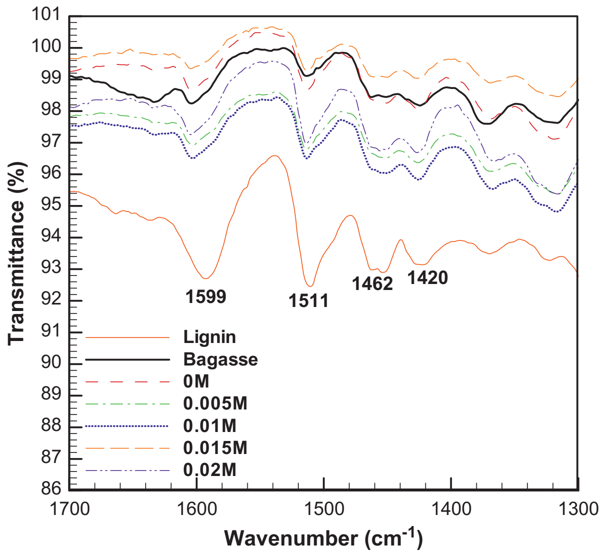

Fig. 8. FTIR spectra of raw bagasse, lignin and pretreated materials at various sulfuric acid concentrations.

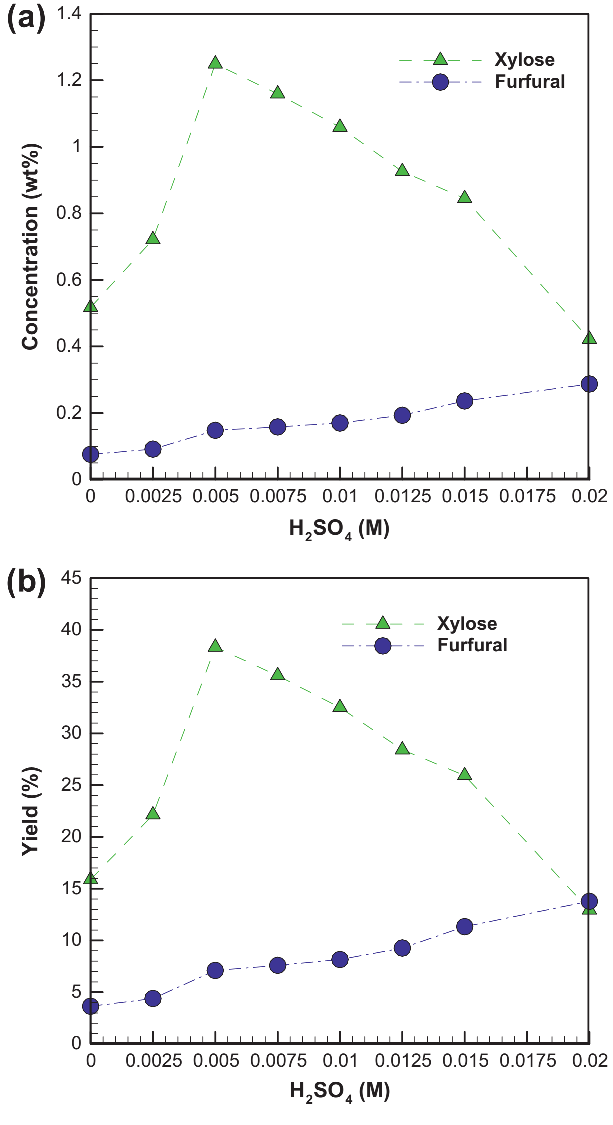

Fig. 9. Distributions of: (a) concentrations and (b) yields of xylose and furfural.

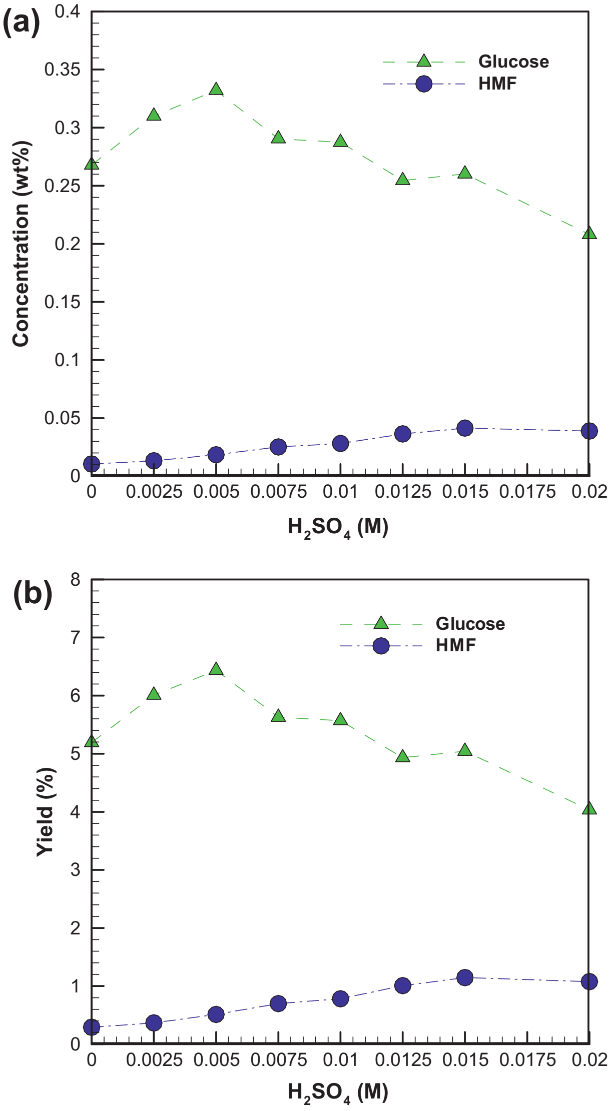

Fig. 10. Distributions of: (a) concentrations and (b) yields of glucose and HMF.

tively. In examining the study of Cámez et al. [40] where 4% (w/w) of H_3PO_4 was used to pretreat bagasse (122 °C for 300 min), the obtained concentrations of xylose and glucose were 17.6 and 3.0 g L^{-1}, respectively. In the study of Pattra et al. [42], 0.5% (v/v) of H_2SO_4 was used to pretreat bagasse (121 °C for 60 min) and the obtained concentrations of xylose and glucose were 11.3 and 11.9 g L^{-1}, respectively. Their concentrations are somewhat higher than the present study; however, the acid concentrations are much higher than the solution of this work, implying that more efforts on corrosion-resistant materials and neutralization prior to fermentation are required.

In Table 3, the hemicellulose conversion physically stands for the total percentage of xylose and furfural converted from hemicellulose; the cellulose conversion designates the total percentage of glucose and HMF converted from cellulose. As seen in Fig. 11a, the maximum conversions of hemicellulose and cellulose are 45.4% and 7.0%, respectively, and they both develop at 0.005 M. This means that xylose and furfural in the hydrolysis products from hemicellulose are around 45 wt%; at the same time, glucose and HMF in the hydrolysis products from cellulose are approximately 7 wt%. Though the furfural yield grows with increasing acid concentration (Fig. 9b), it is noted that the minimum furfural selectivity is located at 0.005 M (Fig. 11b). Alternatively, the higher the acid concentration, the higher the HMF selectivity is. In particular, when the acid concentration reaches 0.02 M, the selectivities of

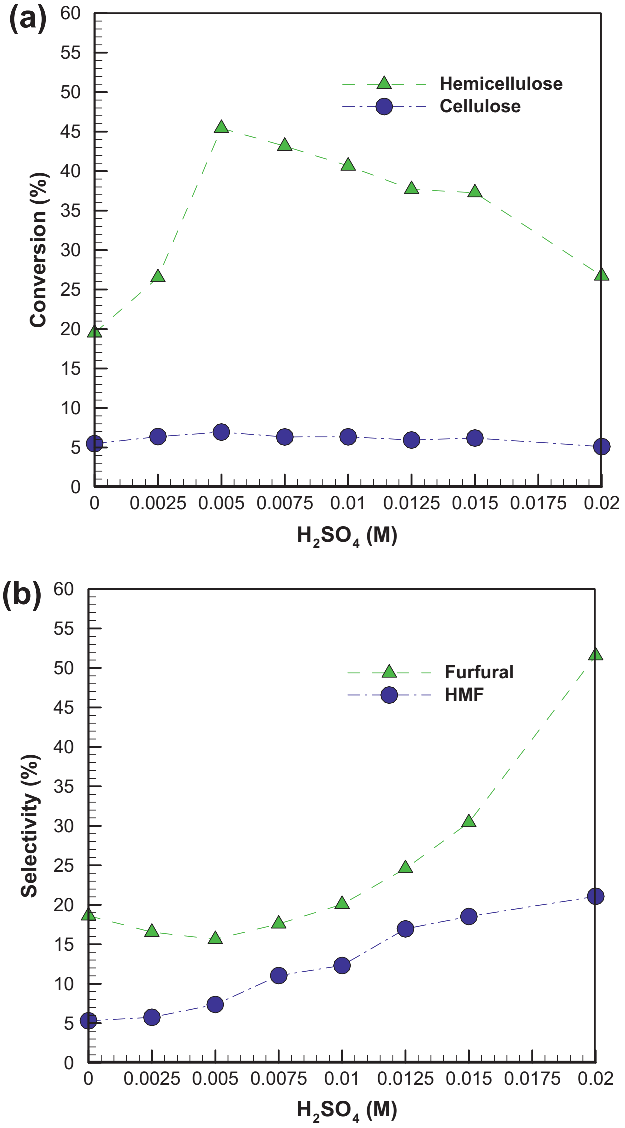

Fig. 11. Distributions of: (a) conversions and (b) selectivities of furfural and HMF.

Table 3
Definitions of yields and conversions of sugars and inhibitors.

Definition (%)	Calculation
Xylose yield	$\frac{\text{xylose(g)}\times 0.88}{\text{hemicellulose in bagasse(g)}}\times 100^{a}$
Glucose yield	$\frac{\text{glucose(g)}\times 0.9}{\text{cellulose in bagasse(g)}}\times 100^{b}$
Furfural yield	$\frac{\text{furfural(g)}\times 1.375}{\text{hemicellulose in bagasse(g)}}\times 100^{c}$
HMF yield	$\frac{\text{HMF(g)}\times l.286}{\text{cellulose in bagasse(g)}}\times 100^{d}$
Hemicellulose conversion	$\frac{\text{xylose(g)}\times 0.88+\text{furfural(g)}\times 1.375}{\text{hemicellulose in bagasse(g)}}\times 100$
Cellulose conversion	$\frac{\text{glucose(g)}\times 0.9+\text{HMF(g)}\times 1.286}{\text{cellulose in bagasse(g)}}\times 100$
Furfural selectivity	$\frac{\text{furfural(g)}\times 1.375}{\text{xylose(g)}\times 0.88+\text{furfural(g)}\times 1.375}\times 100$
HMF selectivity	$\frac{\text{HMF(g)}\times 1.286}{\text{glucose(g)}\times 0.9+\text{HMF(g)}\times 1.286}\times 100$

$C_5H_8O_4$: hemicelluloses; $C_5H_{10}O_5$: xylose; $C_6H_{10}O_5$: cellulose; $C_6H_{12}O_6$: glucose; $C_5H_4O_2$: furfural; $C_6H_6O_3$: HMF.

[a] 0.88 = molecular weight of $C_5H_8O_4$ (molecular weight of $C_5H_{10}O_5$)$^{-1}$.

[b] 0.9 = molecular weight of $C_6H_{10}O_5$ (molecular weight of $C_6H_{12}O_6$)$^{-1}$.

[c] 1.375 = molecular weight of $C_5H_8O_4$ (molecular weight of $C_5H_4O_2$)$^{-1}$.

[d] 1.286 = molecular weight of $C_6H_{10}O_5$ (molecular weight of $C_6H_6O_3$)$^{-1}$.

furfural and HMF are 51.6% and 21.1%, respectively. That is to say, over 50% of xylose and 20% of glucose are transformed to the inhibitors. Summarizing the results obtained in Figs. 9–11, seeing that the maximum yields of xylose and glucose as well as the minimum furfural selectivity occur at 0.005 M, it is concluded that the aforementioned concentration is a feasible condition for bagasse pretreatment and bioethanol production.

4. Conclusions

Sugarcane bagasse pretreated via microwave-assisted heating in a dilute sulfuric acid solution for bioethanol production has been performed in the present study. The heating temperature and soaking time are 180 °C for 30 min, respectively, and the acid concentration is in the range of 0–0.02 M. From the fiber analysis, it is found that around 40–44 wt% of bagasse is degraded from the pretreatment in which around 80–98% of hemicellulose is hydrolyzed. For this reason, the DTG curve evolves from a double-peak distribution to a single-peak one. From XRD and FTIR analyses, it is found that the characteristics of crystalline cellulose and lignin are obviously exhibited, revealing that the two constituents are hardly affected by the pretreatment. On the other hand, the analysis of the liquid solution suggests that the profiles of xylose and glucose yields are featured by a maximum distribution where the maximum value occurs at 0.005 M. In contrast, a higher acid concentration leads to higher yields of furfural and HMF, stemming from the further degradation of xylose and glucose. This is the reason that the yields of xylose and glucose decay when the acid concentration increases from 0.005 to 0.02 M. When the conversions of hemicellulose and cellulose are analyzed, the highest conversions are located at 0.005 M where the lowest selectivity of furfural is also exhibited. From the operating point of view for sugarcane bagasse pretreatment, it is concluded that the optimal acid concentration occurs at 0.005 M along with the heating temperature of 180 °C for 30 min.

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